Cathode Catalyst Layers in PEFC: The Major Competitive Ground

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Outline

I. Introduction

- Why focus on CCL?
- The major competitive ground...

II. Self-Organization in Catalyst Layers

III. Structural Picture and Model of Water Balance

- Three State Model: watershed
- Full Coupling: mass transport vs. partial saturation
- Steady State Diagram: bistability
- Parameter Study: optimization

IV. Conclusions

I. Why focus on catalyst layer?

"Go for the messes – that's where the action is!"

S. Weinberg, *Scientist: Four golden lessons*, Nature 426, 389, 2003.

- ❑ Price and abundance of Pt: feasibility of PEFC
- ❑ Key importance for operation, performance, and design
- ❑ Randomness at multiple scales
- ❑ Lack in systematic understanding & controversial issues
- ❑ Modeling: percolation, agglomerates, macrohom. approach

➔ From optimizing randomness towards rational design!

➔ High electrocatalytic activity with minimal amount of Pt

I. Controversial Issues

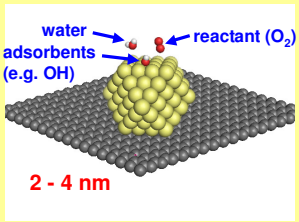
- ❑ Assessment of catalyst utilization (diagnostics)
  - ➔ no "straightforward" technique
- ❑ Nature of electrocatalytically active interfaces
  - ➔ Pt|ionomer, Pt|liquid water or Pt|vapor?
- ❑ Distribution, structure and function of ionomer
  - ➔ needed or abundant?
- ❑ Distribution, structure and function of water
  - ➔ reaction product, proton solvent and asphyxiant
- ❑ Role of porous structure and liquid water accumulation
  - ➔ formation – steady state operation – degradation

How good are the currently used CCL?

I. The Major Competitive Ground in Terms of…

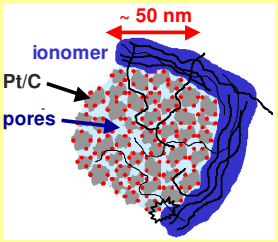
… Structural Complexity: Hierarchy of Scales

Supported nanoparticles



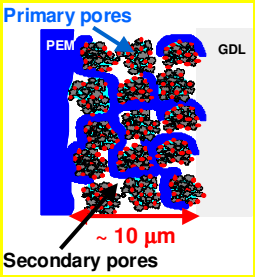
- ❑ S-to-V atom ratio
- ❑ active sites
- ❑ kinetics & activity

Agglomerates



- ❑ formation, composition
- ❑ electrostatic effects
- ❑ effectiveness factor

Composite layer

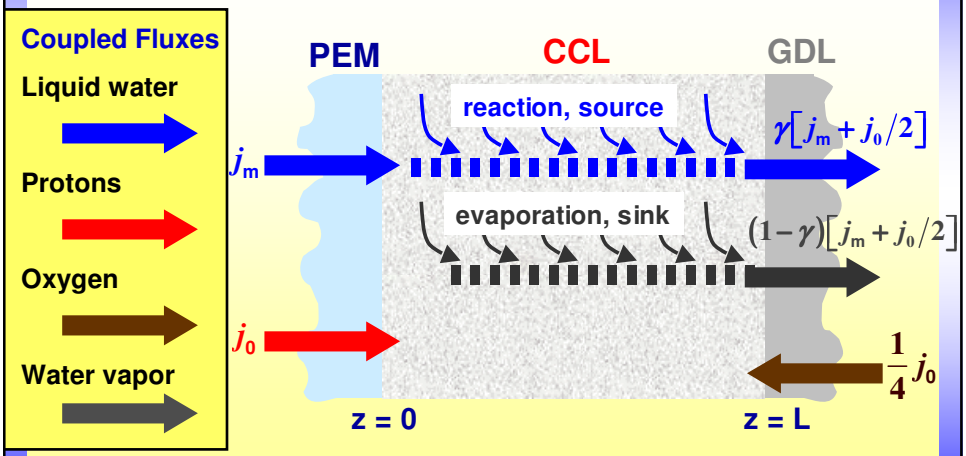


- ❑ network morphology
- ❑ porous structure
- ❑ rate distribution

➔ Catalyst utilization is not a simple "on/off" function
➔ Scales are separable

I. The Major Competitive Ground in Terms of…

… Coupled Processes



I. The Major Competitive Ground in Terms of…

… Performance Optimization

$$j^0 = [m_{Pt}]\, 2 \cdot 10^3\, j^{0*}\, \varepsilon^{S/V}\, \Gamma_a\, g(S_r)\, \frac{f(X_{PtC}, X_{el})}{X_{PtC}}$$

Exchange current density

I. Optimization Problem

large

$$j^0 = [m_{Pt}]\, 2 \cdot 10^3\, j^{0*}\, \varepsilon^{S/V}\, \Gamma_a\, g(S_r)\, \frac{f(X_{PtC}, X_{el})}{X_{PtC}}$$

small

Exchange current density

Losses in voltage efficiency – three causes:

- ❑ activation losses of kinetic processes
- ❑ statistical inhomogeneity
- ❑ non-uniformity of reaction rate distribution

I. Optimization Problem

$$j^0 = [m_{Pt}]\, 2 \cdot 10^3\, j^{0*}\, \varepsilon^{S/V}\, \Gamma_a\, g(S_r)\, \frac{f(X_{PtC}, X_{el})}{X_{PtC}}$$

Exchange current density

Electrocatalysis

- experiments on model catalysts
- electronic structure calculations

Systematic trends due to

- particle size (active sites)?
- shape, composition?
- surface structure?
- substrate effects?

➔ activation losses

I. Optimization Problem

$$j^0 = [m_{Pt}]\, 2 \cdot 10^3\, j^{0*}\, \varepsilon^{S/V}\, \Gamma_a\, g(S_r)\, \frac{f(X_{PtC}, X_{el})}{X_{PtC}}$$

Exchange current density

Electrocatalysis

- experiments on model catalysts
- electronic structure calculations

Systematic trends due to

- particle size (active sites)?
- shape, composition?
- surface structure?
- substrate effects?

➔ activation losses

Statistical Geometry

- particle size effects (surface-to-volume atom ratio)
- phase segregation, agglomeration (electrostatic effects)
- triple phase boundary (percolation effects)
- porous structure, partial saturation

➔ statistical spatial inhomogeneity

I. Optimization Problem

$j^0 = [m_{Pt}]$ x activity x utilization

Exchange current density

Electrocatalysis

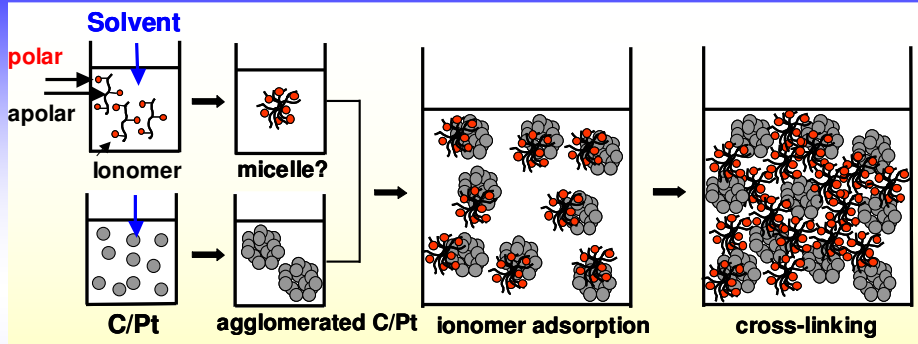
Statistical Geometry

Operation in fuel cell:
complex coupling with transport processes and water balance

➔ non-uniformity of reaction rate distribution
➔ overall effectiveness of catalyst utilization

➔ Key role of composition, porous structure, partial saturation

II. Self-Aggregation in Catalyst Layers



Vary
- composition
- type of carbon
- ionomer
- solvent
- conditions

Control
- agglomeration
- phase segregation
- cross-linking
- pore space morphology
- durability

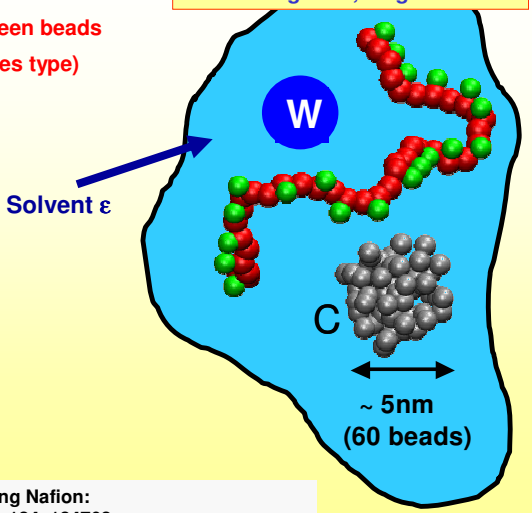
II. Computational Modeling with Coarse-grained MD

Systems at micro-to-meso level

➔ replace components by spherical beads

➔ renormalized interactions between beads
(pair potentials of Lennard-Jones type)

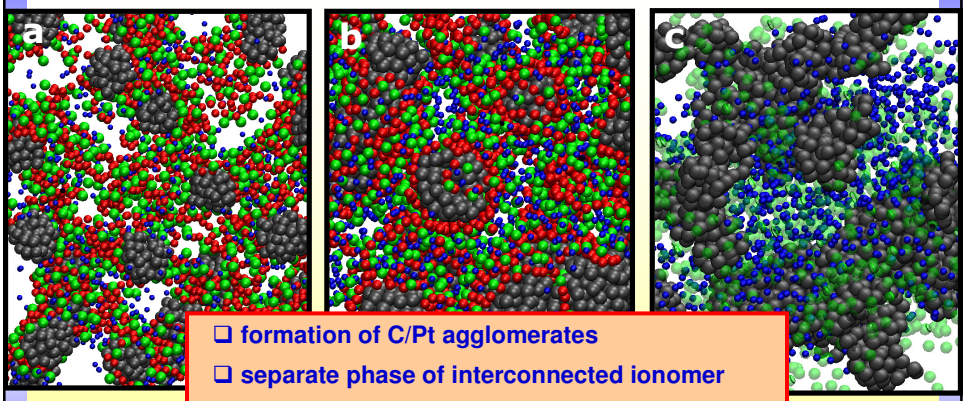
Coarse-grained model of Nafion,
20-unit oligomer, length ~ 30 nm



Coarse-grained approaches for simulating Nafion:
J. T. Wescott et al. 2006, J. Chem. Phys., 124, 134702.
D. Y. Galperin, A. R. Khokhlov 2006, Macromol. Theory and Simul. 15, 137.

II. Formation of Phase-Segregated CCL Morphology

Annealed structure ••••••••••••••••••••••➔ Equilibrated structure



- ❑ formation of C/Pt agglomerates
- ❑ separate phase of interconnected ionomer
- ❑ ionomer backbones attached to C

➡ no penetration of ionomer into agglomerates!

K. Malek, M. Eikerling, Q. Wang,
T. Navessin, and S. Liu, JPC B, accepted.

III. Effects of Composition and Liquid Saturation

$$j^0 = [m_{Pt}]\, 2\cdot 10^3\, j^{0*}\, \varepsilon^{S/V}\, \Gamma_a\, g(S_r)\, \frac{f(X_{PtC}, X_{el})}{X_{PtC}}$$

Interpenetrating networks – volume portions:

X_{PtC}, X_{el}, $X_p = 1 - X_{PtC} - X_{el}$

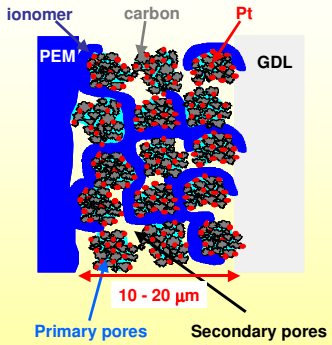
Liquid saturation: $S_r = \frac{1}{X_p}\int_0^{r_c} dr' \frac{dX_p(r')}{dr'}$

Mesoscopic scale:

fraction of wetted Pt $g(S_r) \le 1$

Macroscopic scale:

triple-phase boundary $\frac{f(X_{PtC}, X_{el})}{X_{PtC}} \le 0.3$



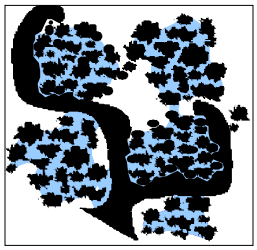
Statistical limit of catalyst utilization in random composites

20-25%

M. Eikerling, A.S. Ioselevich, A. A. Kornyshev, Fuel Cells 4, 131 (2004).
M. Eikerling, *J. Electrochem. Soc.* 153, E58 (2006).

III. Effects of Porous Structure and Water Balance

Partially saturated porous medium



activity vs. transport

Two-level approach

composition & structure

↓

effective properties (in REVs)

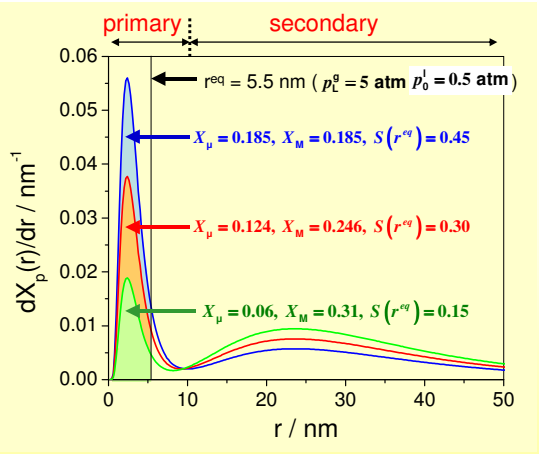
↓

performance

M. Eikerling, *J. Electrochem. Soc.* 153, E58 (2006).

III. From Structural Picture to Model of Water Balance

Bimodal log-normal pore size distribution



Capillary equilibrium controls pore filling – significance of wetting angle

$$p^c = \frac{2\sigma\cos(\theta)}{r_c} = p^g - p^l$$

Laplace eq.

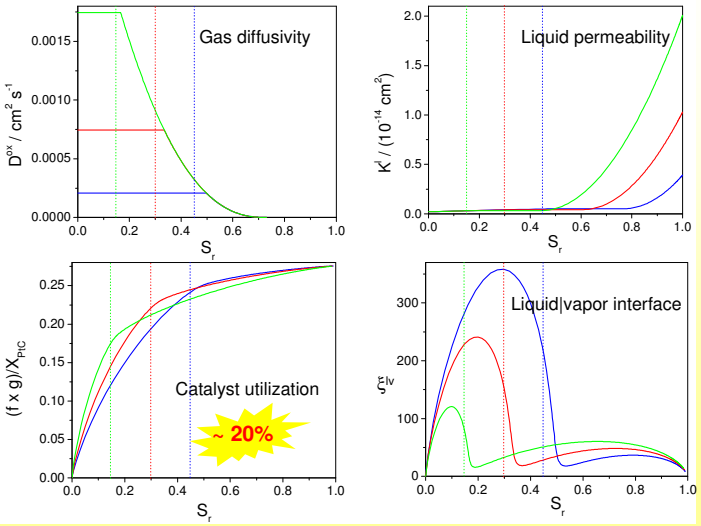
III. Effective Properties

Low saturation	**High saturation**
j^0, K – small	j^0, K – large
D^o, ξ^{liv} – large	D^o, ξ^{liv} – small

Mass transport

vs.

Kinetics



III. Transport and Reaction in CCL – Conservation Laws

General form of the continuity equation: $\cancel{\frac{\partial \rho(\vec{r},t)}{\partial t}} + \nabla \cdot \vec{j}(\vec{r},t) = Q(\vec{r},t)$

Consider steady state operation, neglect gas convection:

φ – el. potential $\frac{d^2\varphi(z)}{dz^2} = \frac{1}{\sigma_{el}} Q^{ec}(z)$

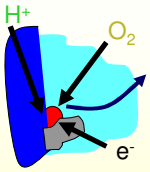
p – ox. pressure $4fD^{o}(S_r)\frac{dp(z)}{dz} = j_0 - j^{p}(z)$

q – vapor press. $-f\frac{d}{dz}\left[D^{v}(S_r)\frac{dq(z)}{dz}\right] = Q^{lv}(z)$

p^l – liquid press. $\frac{F}{V_m \mu^l} K^{l}(S_r)\frac{dp^{l}(z)}{dz} = \left(n+\frac{1}{2}\right) j^{p}(z) + j^{v}(z) - j_m - \frac{j_0}{2}$

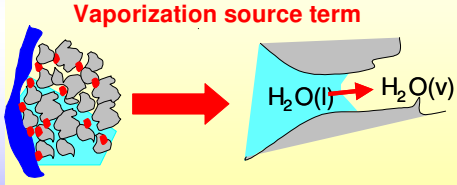
III. Source Terms

Electrochemical source term



$Q^{ec}(z) = \frac{j^{0}(S_r)}{L}\frac{p(z)}{p_L}\exp(\alpha f \varphi(z))$

Vaporization source term



$Q^{lv}(z) = \frac{e_0 \kappa^{e}}{L}\xi^{lv}(S_r)\{q_r^{s}(T) - q(z)\}$

with saturated vapor pressure (Kelvin equation)

$q_r^{s}(T) = q^{s,\infty}(T)\exp\left(-\frac{2\sigma\cos(\theta)V_m}{RTr_c}\right),\ q^{s,\infty}(T) = q^{0}\exp\left(-\frac{E_a}{k_B T}\right)$

III. Modeling Strategy: Two Main Steps

Porous Structure
PSD
Saturation
$S_r(z)$

Effective Properties
$D^{\circ}(S_r(z))$, $D^{v}(S_r(z))$
$K^{l}(S_r(z))$
$j^{0}(S_r(z))$
$\xi^{lv}(S_r(z))$

Local Variables

Electrode potential: $\varphi(z)$, $\eta(z)$

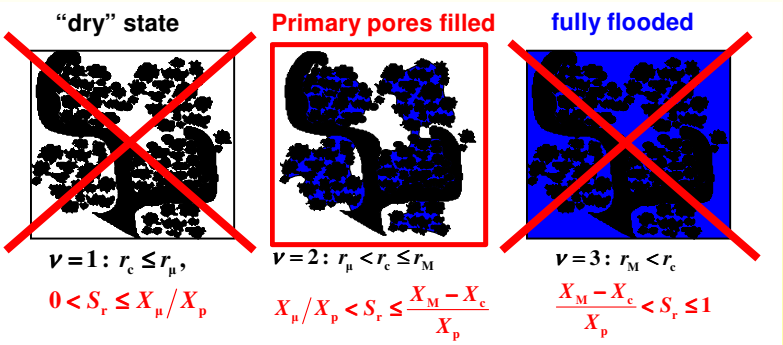
	O_2,	$H_2O(g)$,	$H_2O(l)$
Pressures:	$p(z)$,	$q(z)$,	$p^{l}(z)$
Fluxes:	H^+,	$H_2O(g)$,	$H_2O(l)$
	$j_p(z)$,	$j^{v}(z)$,	$j^{l}(z)$

Liquid saturation: $S_r(z)$

Global Performance
➔ catalyst utilization
➔ voltage efficiency
➔ water balance

III. Previous Results: Three State Model

Simplistic psd (δ-distribution): $\frac{dX_p(r)}{dr} = X_{\mu}\delta(r-r_{\mu}) + X_M\delta(r-r_M)$



Constant coefficients in each state! – Analytical solutions can be obtained.
Focus on operation in intermediate state.

III. Three State Model: Main Insights

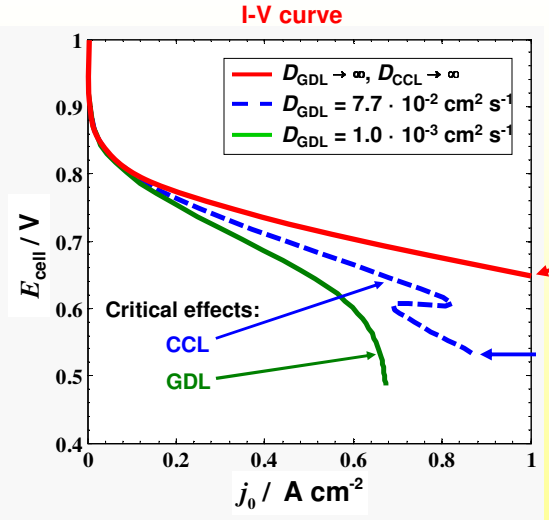
CCL acts like a watershed in the cell

- ❑ controls water fluxes and vaporization in PEFC
- ❑ prone to flooding at relevant current densities
- ❑ porous structure and liquid saturation are key

Sensitive dependences of performance on parameters

- ❑ **structure:** thickness, psd, wetting angle
- ❑ **operation:** water flux from PEM, gas/liquid pressures

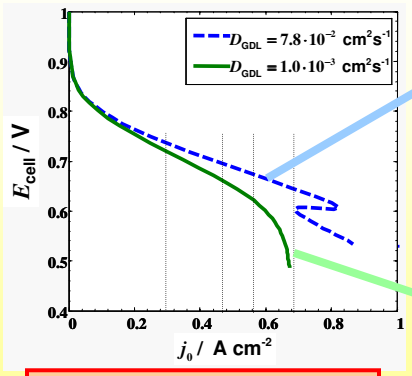
III. Full Coupling: Water Formation – Where?

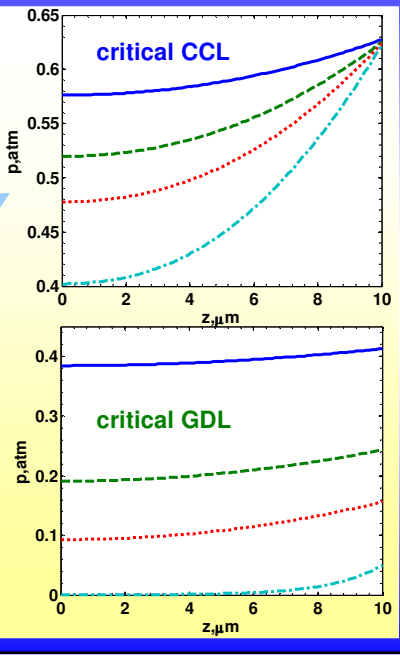


ideal case:
uniform utilization

real case:
- ❑ performance losses
- ❑ nonlinear effects
- ❑ failure modes

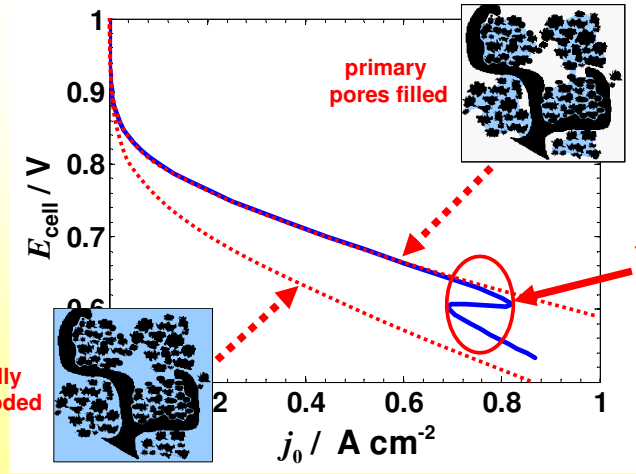
III. Oxygen Distribution in CCL





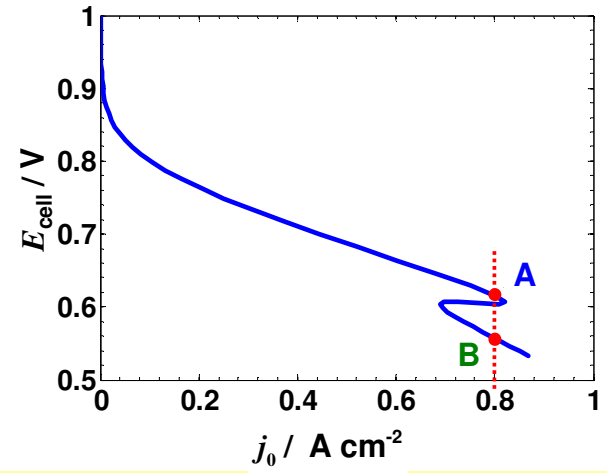
Active vs. inactive medium:
different signatures
of water accumulation!

III. Current-Voltage Curve



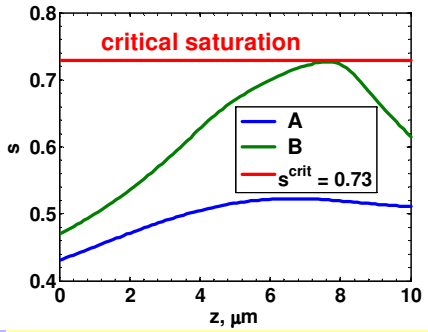
… interplay between liquid saturation and oxygen starvation!
Effect of nonuniform, critical liquid water formation!

III. Transition Region: Steady State Multiplicity

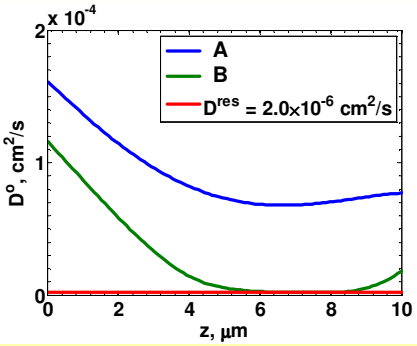


III. Transition Region: Coexisting States

Liquid saturation

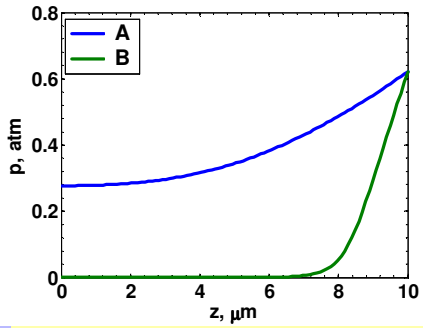


Oxygen diffusion

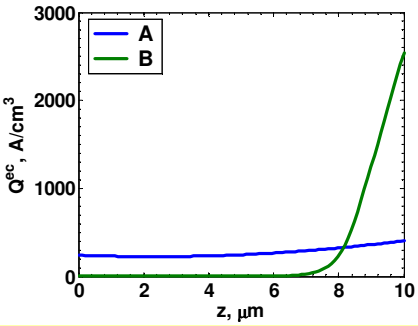


III. Transition Region: Coexisting States

Oxygen partial pressure

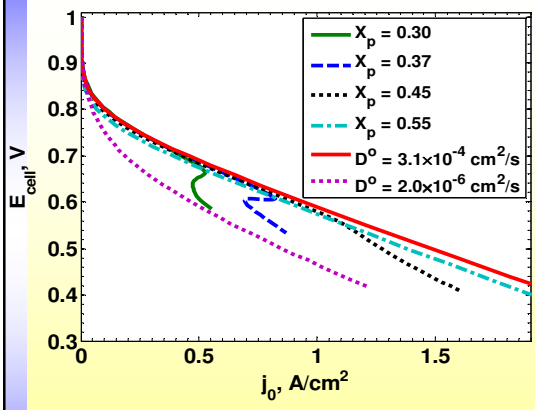


Reaction rate distribution



Transition from uniform to non-uniform reaction rate distribution due to coupling between liquid water saturation and oxygen transport

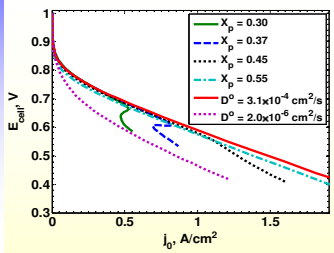
III. Parameter Study: Total Porosity



Total porosity > 45% sufficient

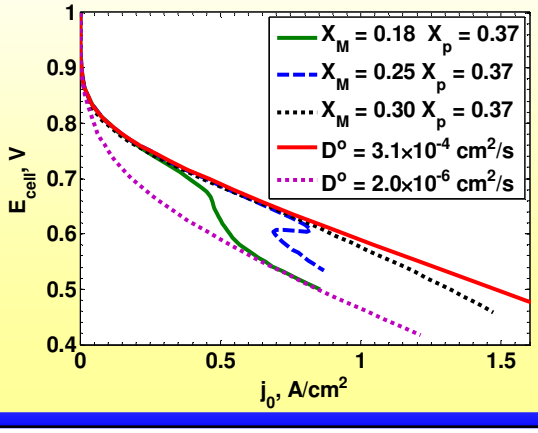
III. Parameter Study: Pore Space Morphology

Total porosity

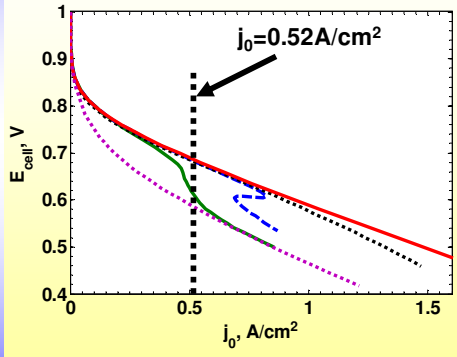


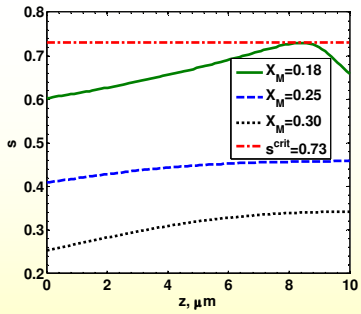
Secondary pores (between agglom.) are vital

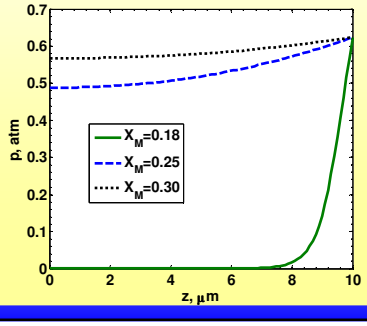
Volume fraction of secondary pores



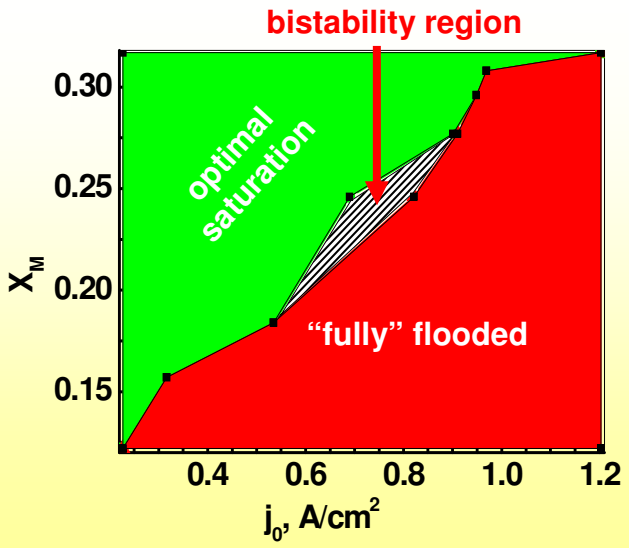
III. Parameter Study: Pore Space Morphology





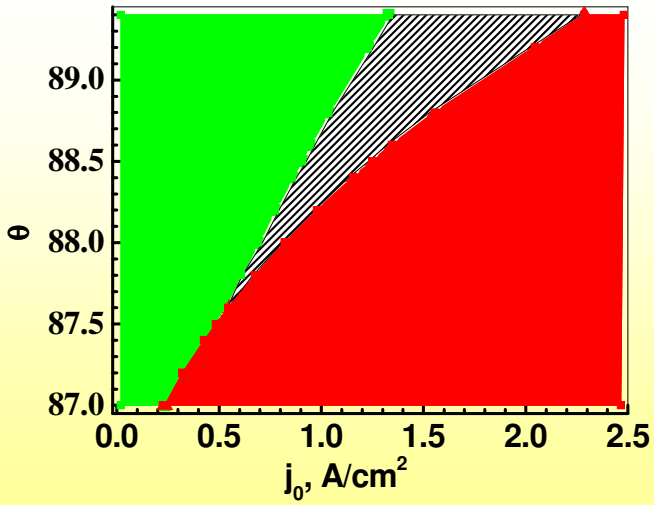


III. Steady State Diagram – Fraction of Second. Pores



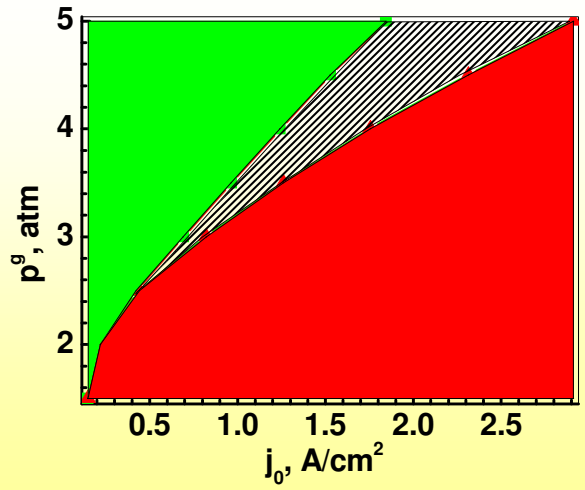
➔ tool for evaluating CCL design

III. Steady State Diagram: Wetting Angle



Important parameter – difficult to control!

III. Steady State Diagram: Total Gas Pressure



III. Main Results

Composite porous structure

Effective properties

Operating conditions

Performance, water balance

Role of bimodal psd: controls distinct functions

- ❑ small pores: active area ➔ hydrophilic
- ❑ large pores: mass transport & water balance ➔ hydrophobic
- ❑ affects uniformity of reaction rate distribution

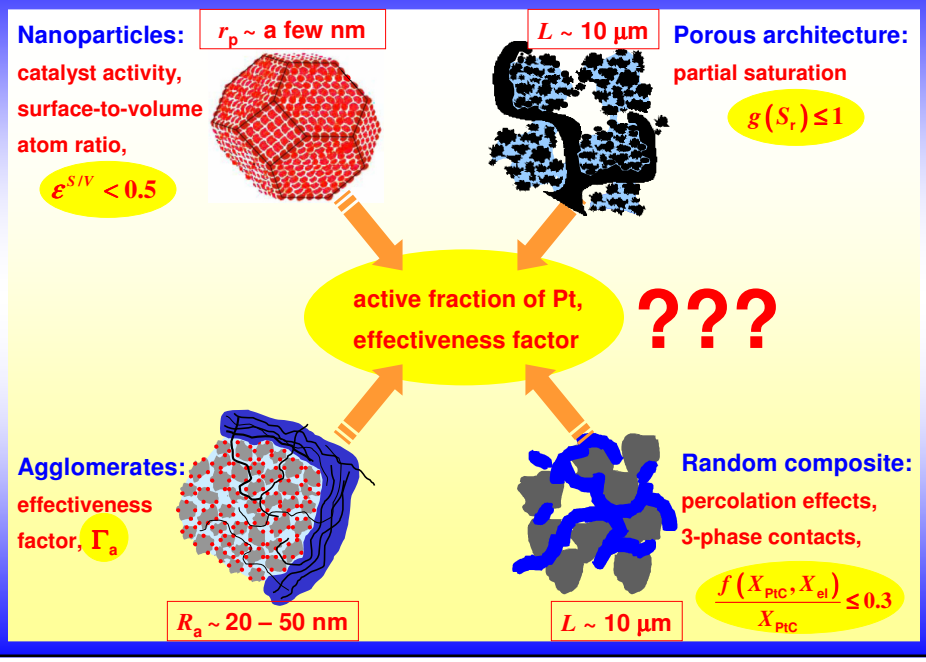
Interplay between oxygen transport and water accumulation

- ❑ distinct signatures of CCL and GDL
- ❑ critical conditions in CCL: bistability in I-V curves
- ❑ main parameters: X_M, X_p, θ, p^g

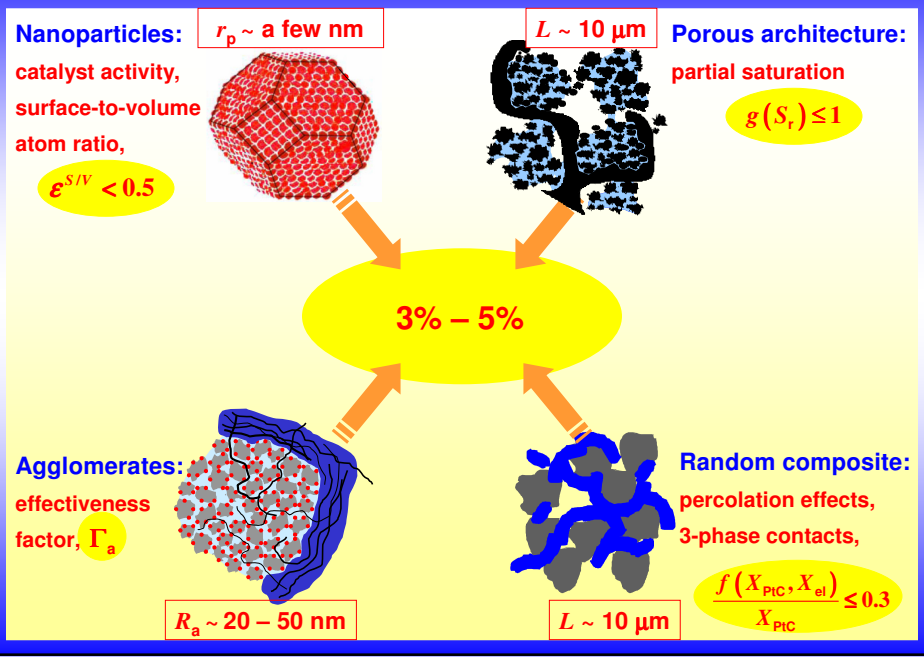
IV. Outlook

- ❑ Theoretical understanding: water accumulation vs. mass transport
- ❑ More detailed characterization of wetting properties
- ❑ Water distribution and structure (surface – bulk, ionomer - pores)
- ❑ Validate and refine parameterization of effective properties
- ❑ Coupling to water balance in other components
- ❑ Evaluate CCL design options
  - ➔ improvement of current design?
  - ➔ radically new design?
  - ➔ don't forget about porous structure and water balance
- ❑ Linking the scales: from structure formation to performance

Active Catalyst Sites: Multiple Scales



Active Catalyst Sites: Multiple Scales



Reference Parameters Used in Calculations

$L, \mu m$		10	Thickness of CCL
$L_{PTL}, \mu m$		125	Thickness of PTL
X_{ptc}		0.3	Volume fraction of Solid phase
X_{el}		0.33	Volume fraction of electrolyte
$X_p = 1 - X_{ptc} - X_{el}$		0.37	Volume fraction of void space
Psd#2	X_μ	0.124	Volume fraction of primary pores
	X_M	0.246	Volume fraction of secondary pores
$T, °C$		60	Temperature
p^g, atm		3.0	Total gas pressure
p_{GDL}, atm		0.63	Oxygen pressure
θ, deg		88	Contact angle of pore and water system
$D^{res}, cm^2/s$		2.0×10^{-6}	Residual gas diffusivity